

# Cathodoluminescence and photoluminescence in the core region of $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{SiO}_{20}$ crystals

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Cathodoluminescence and photoluminescence of  $\text{Bi}_{12}\text{SiO}_{20}$  and  $\text{Bi}_{12}\text{GeO}_{20}$  samples are studied. Both kinds of samples show a dark orange central part or core. Emissions in the blue, green, and red spectral regions are observed. The 640 nm band is the predominant feature in the core emission. The evolution of this band during electron irradiation suggests possible emission mechanisms. In addition, two infrared emissions at about 915 and 1390 nm are detected. © 1996 American Institute of Physics. [S0021-8979(96)05109-2]

## INTRODUCTION

The phase diagram of  $\text{Bi}_2\text{O}_3\text{--MO}_2$  ( $M=\text{Ge, Si, Ti}$ ) gives stable compounds with ratios of 1:3, 2:3, and 6:1. Consequently, the compounds are  $\text{Bi}_2\text{M}_3\text{O}_9$ ,  $\text{Bi}_4\text{M}_3\text{O}_{12}$ , and  $\text{Bi}_{12}\text{MO}_{20}$ .<sup>1</sup> For technological applications, the best known is  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , which is a scintillator material. The sillenite family formed by  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO),  $\text{Bi}_{12}\text{GeO}_{20}$  (BGO), and  $\text{Bi}_{12}\text{TiO}_{20}$  (BTO) is widely employed in different advanced technological applications.<sup>2</sup>

All of these compounds can be considered as a stabilized form of  $\gamma\text{-Bi}_2\text{O}_3$ . Thus, some properties are a consequence of the presence of the  $\text{Bi}_2\text{O}_3$  group. For example, the luminescence peak around 500 nm is associated with the intraionic transition of  $\text{Bi}^{+3}$  which is present in  $\text{Bi}_2\text{Ge}_3\text{O}_9$ ,<sup>3</sup>  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ,<sup>4</sup>  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals doped with Mn,<sup>5</sup> BGO and BSO,<sup>6</sup> BGO doped with Ho,<sup>7</sup> etc.

These materials are prepared by the Czochralski (Cz) method from stoichiometric starting materials, with the exception of BTO crystals which require a flux of nonstoichiometric composition as a starting material. Crystals obtained by the Cz method are of high quality, except for the possible appearance of a distorted central region along the pulling direction. The central part or core contains a high concentration of voids in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals,<sup>8</sup> and has a dark orange color in the sillenite family. From the point of view of technological applications, the presence of a core region is undesirable. For this reason, core phenomena have been extensively studied in crystals grown under different conditions. Although there is no general agreement, three major conclusions can be deduced from the previously published results:

(i) the composition or ratio of Bi to M in the core, is equal to that in the regions outside the core;<sup>9,10</sup> (ii) the origin of the core is a consequence of a nonplanar solid–liquid interface during growth, with the appearance of facets;<sup>11,12</sup> and (iii) the concentration of intentional or unintentional impurities in the core is higher compared to the regions outside the core.<sup>13</sup> In this paper, we have studied the core regions in BGO and BSO crystals by means of the cathodoluminescence (CL) and photoluminescence (PL) techniques.

## EXPERIMENT

BGO and BSO crystals have been grown by the Cz technique. The details of the equipment and growth experiments have been previously described.<sup>12,14</sup> The starting materials were pure  $\text{Bi}_2\text{O}_3$  and  $\text{GeO}_2$  or  $\text{SiO}_2$  (J. Matthey, Grade A1). The crystals were grown in a resistance furnace in Pt crucibles, under atmospheric conditions with growth parameters appropriate to yield a central core. The samples were cut from the ingot, perpendicular to the growth direction. After polishing with  $\text{Al}_2\text{O}_3$  abrasive powder, they were studied by PL and CL techniques.

Steady state PL, time resolved spectra (TRES), and lifetime (LT) measurements were performed using a CD900 spectrometer system from Edinburgh Instruments, with a R955 photomultiplier in a Peltier cooled housing. The IR emission spectra in the range of 0.8–1.8  $\mu\text{m}$  were obtained using a germanium detector (North Coast EO-817L). The excitation source was a 450 W Xe lamp for steady state spectral measurements and a 1  $\mu\text{s}$  Xe flashlamp for TRES and LT. The samples were cooled in a closed helium cry-

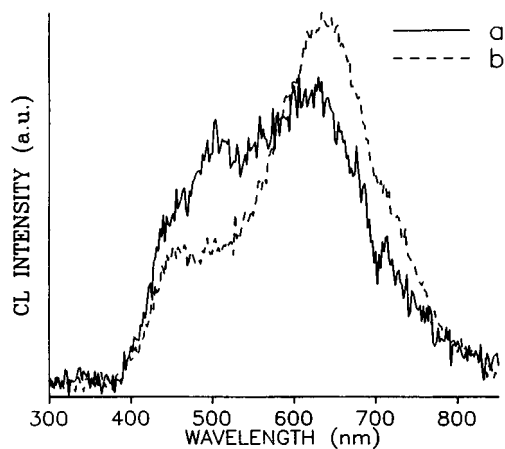


FIG. 1. Typical CL spectra of (a) yellow region and (b) the core of BGO samples.

ostat. The CL measurements were carried out in a Hitachi S-2500 scanning electron microscope. The experimental setup for CL measurements consists of an optical lens that focuses the light on a guide. A computer controlled Oriel 77200 monochromator and a Hamamatsu R928 photomultiplier were used. CL spectra were recorded at 100 K with a 30 kV beam accelerating voltage. A thin carbon film was deposited in all the samples to avoid charge effects.

## RESULTS

Both kinds of samples show a yellow pale color and a dark orange region, hereinafter called the core. These zones were spectroscopically studied by PL and CL.

CL spectra for  $\text{Bi}_{12}\text{GeO}_{20}$  (BGO) samples are of comparable total intensity in both regions but with different spectral distribution. The yellow region is characterized by two wide bands peaked at about 500 and 620 nm, respectively [Fig. 1(a)]. In the core an emission of about 640 nm is the predominant feature. In addition to a 500 nm emission, also present in the yellow region, a blue contribution peaked at 456 nm is observed in the core spectra causing the flat appearance of this band [Fig. 1(b)]. The CL emission for  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) samples is very weak out of the core showing a band peaked at about 600 nm. In the core the total CL emission increases considerably due to an intense band peaked at about 625 nm. A weak 425 nm band is also observed. Spectra of BSO samples are shown in Fig. 2. In all cases decreasing the excitation density, by defocusing the electron beam, the red emission is enhanced.

From the CL measurements some results, common to both materials, are obtained: the red band in the core presents a higher intensity than in the yellow region and a shift to lower energies. The core also contributes to the spectra with blue emission peaked at about 420 nm for BSO and at 456 nm for BGO. Out of the core the BSO specimens do not show blue emission while a wide band centered at 500 nm is present in all BGO spectra. Total CL emission is higher for BGO samples.

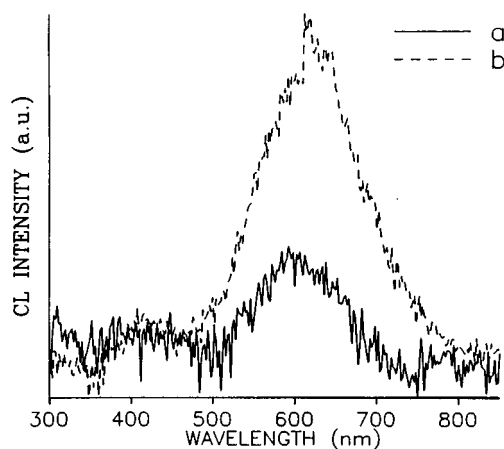


FIG. 2. CL spectra of (a) yellow region and (b) core of BSO samples.

Regions out of the core in both samples were irradiated with 30 kV electrons for 90 min in the scanning electron microscope. CL spectra after irradiation were recorded as shown in Fig. 3. These spectra show in both cases that the red band is enhanced by irradiation. The irradiated area presents a dark orange color as in the core.

Emissions at 450 and 640 nm are detected by PL on BGO samples (Fig. 4). The lifetimes of both emissions at 10

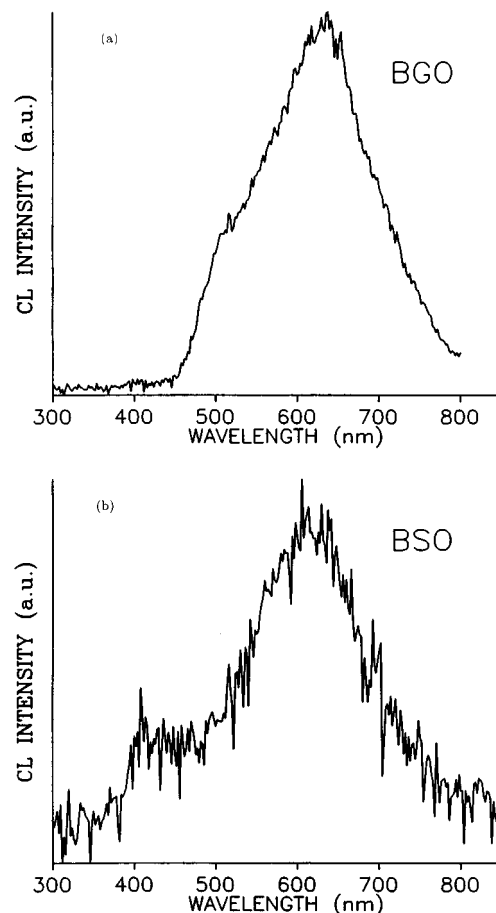


FIG. 3. CL spectra of (a) BGO and (b) BSO yellow irradiated regions.

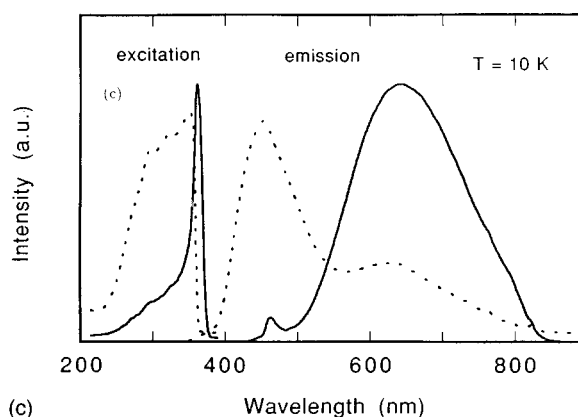
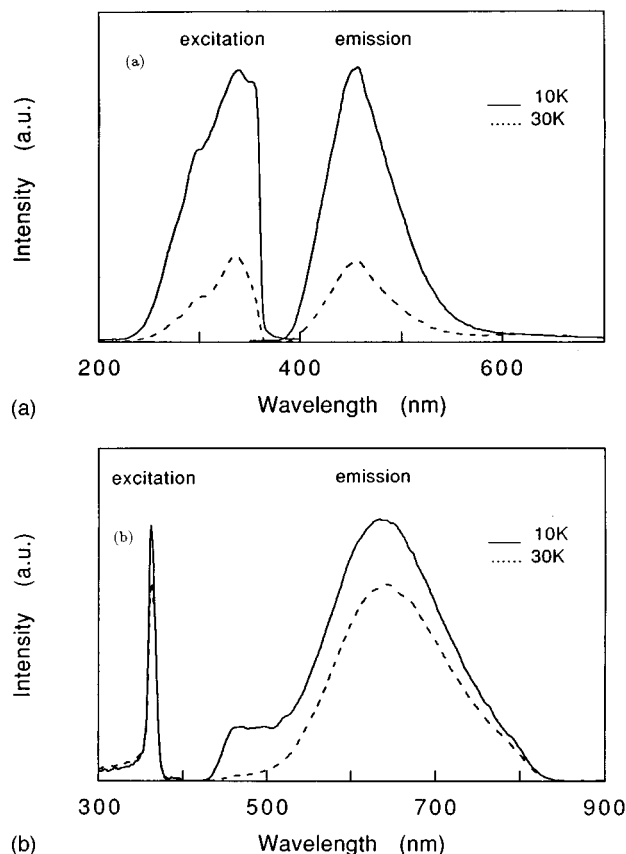


FIG. 4. (a) Excitation and emission PL spectra of the blue band at 10 and 30 K of the yellow BGO areas. (b) Excitation and emission PL spectra of the red band of the yellow BGO areas at 10 and 30 K. (c) Excitation and emission PL spectra of the BGO core.

K were found to be 175 and 145  $\mu$ s, respectively. The excitation spectra differ for these bands as Fig. 4 shows. The blue band is mainly excited by 340 nm light while the red one is excited by 364 nm light. Spectra of the yellow region are independently represented because of the different intensities of the blue and red emissions [Figs. 4(a) and 4(b)]. The ratio between the peak intensity of the blue to the red band is 4 at 10 K. In the core, both emissions have comparable intensities [Fig. 4(c)], showing an increased red band compared with the same emission in the yellow region, in agreement with the CL results. Both bands have a thermal quenching of 20 and 65 meV at 30 and 100 K, respectively. The evolution of the integrated intensity with temperature of both emissions is shown in Fig. 5. The peak energy and width of the blue band remain constant with temperature. On the contrary the red band shifts from 1.93 and 525 meV width at 10 K to 2 eV and 770 meV width at 150 K.

In BSO specimens, PL emission differs from that of BGO. The blue emission is hardly detected and the red emission shifts not only with temperature but also with the excitation wavelength. Spectra of the yellow region are shown in Fig. 6(a) and the evolution of the integrated intensity and peak position with temperature are shown in Fig. 6(b). In the core, the red PL shows no peak displacement relative to the matrix. Two infrared emissions are also detected at 915 and 1390 nm, presenting a 0.4 and 0.2 eV half-width and a thermal quenching with an activation energy of 40 meV [Figs. 7(a) and 7(b)]. These emissions do not depend on the sample or region considered.

## DISCUSSION

The center responsible for the red emission is found in higher concentrations in the core of BGO and BSO samples. The red peak shifts to higher energies in the yellow regions which could be explained in terms of the different environment of the same center in and out of the core. This region is formed by facet growth<sup>6</sup> and probably some remanent impurities from the starting materials aggregate here preferentially producing some stress in the BMO lattice.

In previous studies the center related to the 640 nm (1.95 eV) emission has been proposed to be highly localized. A

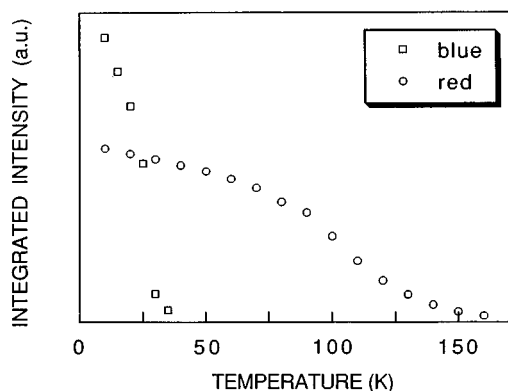


FIG. 5. Evolution of the blue and red band integrated intensities with temperature for BGO samples.

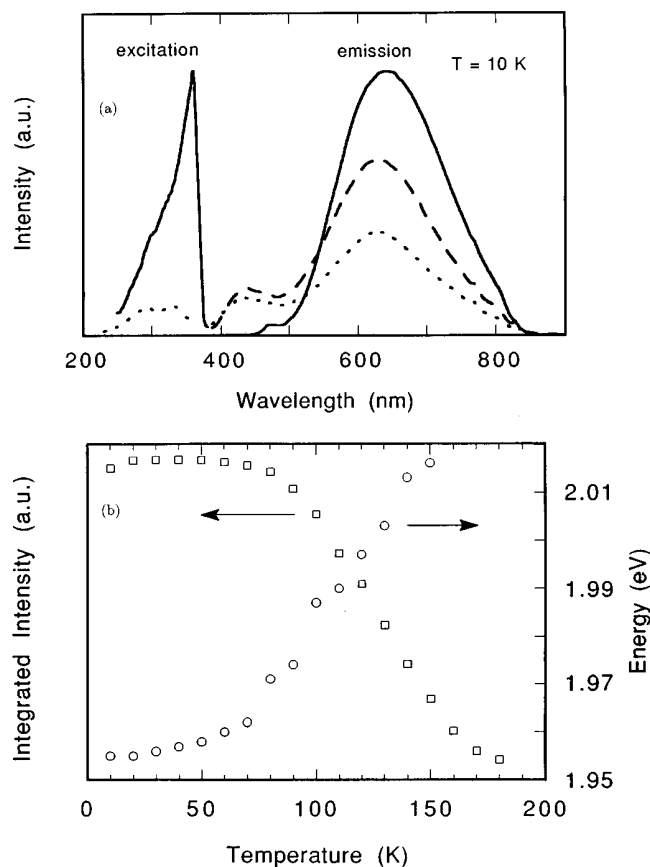


FIG. 6. (a) Excitation and emission spectra of BSO yellow regions. The solid line spectrum corresponds to excitation at 364 nm, the dashed line spectrum to 340 nm, and the dotted line spectrum to 300 nm excitation; (b) temperature dependence of the integrated band intensities of BSO samples.

peak at 1.95 eV in BGO has been related by Grabmaier *et al.*<sup>6</sup> to phosphor doping. Lauer<sup>15</sup> suggests a resonance transfer mechanism from excitons to the luminescence center for this emission detected in undoped samples, but the nature of this center remains unknown.<sup>16</sup>

Our electron irradiation experiments out of the core for both kinds of samples show that by irradiation it is possible to create a “core” with the same orange color as that of the core formed during the crystal growth. Spectra of CL emission in the irradiated regions are shown in Fig. 3. Compared to the unirradiated spectra of Figs. 1(a) and 2(a), the red emission appears enhanced and shifted to 640 nm, as in the core. This indicates that by irradiation it is possible to create out of the core the same center that is responsible for the red emission in the core. This result suggests some possibilities for the center responsible for the 640 nm emission: (1) an ionized impurity, (2) a color center. Possible candidates for the first suggestion are impurities as Cr or Fe,<sup>6</sup> which create an absorption band in the orange–red region of the visible spectrum. These impurities are present with higher concentrations in the core than outside, as has been demonstrated for the case of Fe.<sup>10</sup> Although these impurities are unintentionally present in starting materials, it is known that they easily diffuse through the crucible wall, and can get incorporated into a nominally pure crystal. This drawback can be avoided when the same crucible is reused at least four times

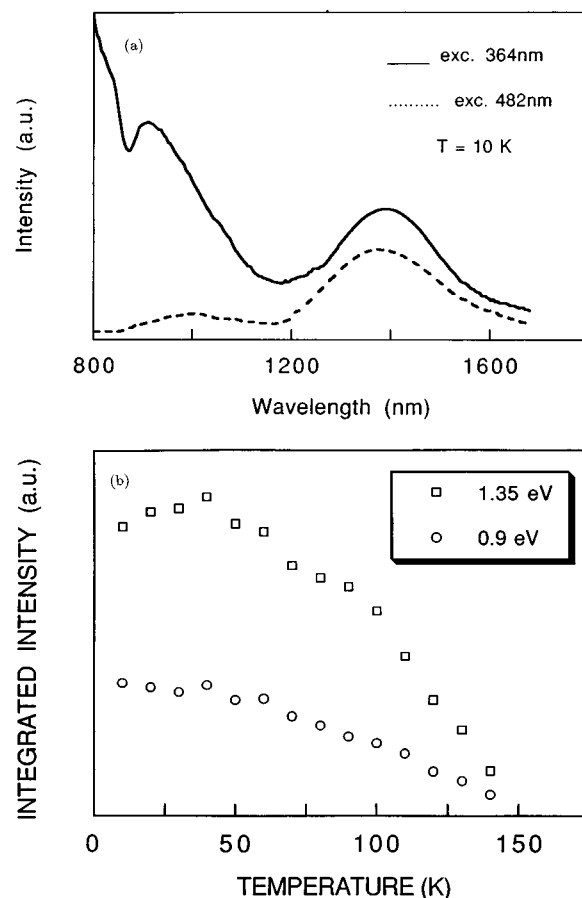


FIG. 7. (a) Emission spectra of the infrared bands detected in both regions and samples. (b) Evolution with temperature of the integrated intensities of the infrared bands.

with pure starting material. On the other hand, either oxygen vacancies ( $V_O$ ), or complexes formed by Ge or Si vacancies ( $V_{Ge}$ ,  $V_{Si}$ ) with  $V_O$  can be present. In the first case, the  $V_O$  are able to trap electrons to form  $F$  centers, and in the second case the complexes  $V_{Ge}-V_O$  or  $V_{Si}-V_O$  are able to trap holes creating  $V$  centers. In the first case, the oxygen vacancy acts as a doubly positive charged center, and in the second case the complexes act as quadruple negative charged centers which act as donor centers responsible for the  $n$ -type photoconductivity.<sup>3,15,17,18</sup> The concentration of the 640 nm related defect is higher in the core and possibly it presents different charge states outside and in the core region. This would explain the peak position shift and the irradiation-induced emission out of the core. Two possibilities arise: either some impurity can be present in more than one valence state, or Bi is in another charge state. The first possibility has been previously associated with Fe impurity. For the second possibility, it is necessary to take into account that the Bi/Si ratio in the core and out of the core seems to remain constant. Nevertheless, it has been proposed<sup>13</sup> that in BGO/BSO crystals, not only Bi atoms but also  $Bi^{+3}$  and  $Bi^{+5}$  ions can occupy the position of Ge/Si vacancies. These ions could be responsible for the irradiation effect in the regions out of the core, and although the total amount of both ions in and out of the core remain constant, the ratio between

them would change with the irradiation time.

The blue and green emissions described here have been previously reported,<sup>6</sup> but their origin is unknown. The CL results show that the blue contributions in both materials are core related. In BSO the 420 nm emission is also created by irradiation out of the core while with the same treatment of BGO samples the blue emission present in the core does not appear. This suggests that different centers are responsible for the blue emission in BGO and BSO. The different behavior of the 450 nm PL emission for both materials supports the last statement.

With reference to the IR emissions, the 915 nm (1.3 eV) band is attributed by Lauer<sup>15</sup> to a complex of oxygen and Ge or Si vacancies while the 1390 nm (0.9 eV) band is to our knowledge reported for the first time.

## CONCLUSIONS

Luminescence emission in the core region of BGO and BSO is dominated by a band centered at about 640 nm. Outside the core region, the 640 nm emission has been found to increase during irradiation in the scanning electron microscope. It is proposed that the core emission is due either to an ionized impurity such as Cr, Fe, or Bi ions in Ge/Si sites, or to vacancy complexes forming color centers. A blue emission band has been found to be core related.

## ACKNOWLEDGMENTS

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